

ABSTRACT OF THE DISCLOSURE

A new polymerization process (atom transfer radical polymerization, or ATRP) based on a redox reaction between a transition metal (e.g., Cu(I)/Cu(II)), provides "living" or controlled radical polymerization of styrene, (meth)acrylates, and other radically polymerizable monomers. Using various simple organic halides as model halogen atom transfer precursors (initiators) and transition metal complexes as a model halogen atom transfer promoters (catalysts), a "living" radical polymerization affords (co)polymers having the predetermined number average molecular weight by  $\Delta[M]/[I]_0$  (up to  $M_n > 10^5$ ) and a surprisingly narrow molecular weight distribution ( $M_w/M_n$ ), as low as 1.15. The participation of free radical intermediates in ATRP is supported by end-group analysis and stereochemistry of the polymerization. In addition, polymers with various topologies (e.g., block, random, star, end-functional and in-chain functional copolymers [for example, of styrene and methyl (meth)acrylate]) have been synthesized using the present process. The polymeric products encompassed by the present invention can be widely used as plastics, elastomers, adhesives, emulsifiers, thermoplastic elastomers, etc.

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